

Surface photo-oxidation and photostabilization of photocross-linked polyethylene

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Abstract

The surface photo-oxidation and photostabilization of photocross-linked polyethylene (XLPE) have been studied by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The FTIR and XPS data gave the evidence that the surface photo-oxidation of XLPE increases, apparently, with increasing UV-irradiation time. The main photo-oxidation products have been identified as hydroperoxides and various carbonyl compounds. The photostabilization of XLPE can be carried out by suitable pre-irradiation of low-pressure mercury (LPM) lamp and by addition of hinder amine light stabilizers (HALS). The FTIR and XPS data also show that the optimum time of pre-irradiation of LPM lamp is 10 s under the experimental conditions of the present study. The addition of HALS into PE resin can protect the XLPE efficiently from surface photo-oxidation in the photocross-linking process of PE. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Photocross-linked polyethylene; Surface photo-oxidation; Photostabilization; Surface deoxidation; HALS; FTIR; XPS

1. Introduction

In recent years, there have been significant breakthroughs in the photoinitiated cross-linking of thick samples of polyethylene [1–4] and industrial applications of insulated photocross-linked polyethylene (XLPE) wire and cable [5–8]. The mechanism and cross-link microstructures of the photocross-linking of LDPE and its model compounds have been studied by spin-trap electron spin resonance [9–10] and ^{13}C nuclear magnetic resonance [11]. However, UV irradiation of PE by high pressure mercury (HPM) lamp can not only initiate the cross-linking reactions, but also cause photo-oxidation degradation, especially the surface photo-oxidation, which further affects the thermal aging stability of the photocross-linked XLPE materials. In fact, the surface photo-oxidation during the photocross-linking process of PE initiated by the HPM lamp has become a main problem in developing industrial applications of photocross-linking technique.

In the present work, we have studied the surface photo-oxidation products of photocross-linked XLPE

by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). At the same time, the photostabilization of XLPE can be done by the surface deoxidation with the pre-irradiation of low-pressure mercury (LPM) lamp before photocross-linking of PE with the HPM lamp. The photostabilization of XLPE can also be done by addition of hinder amine light stabilizers (HALS). The purpose of this work is to clarify the formation mechanism of surface photo-oxidation products and to search for effective methods of photostabilization in the photoinitiated cross-linking of PE.

2. Experimental

2.1. Materials

The LDPE resin (112A-1, MI=2.0) from Yanshan Petrochemical Co., Ltd., China was used in the present work. Photoinitiator benzophenone (BP) from Shanghai Reagent Factory No.1 (Chemical pure) and crosslinking agent triallyl isocyanurate (TAIC) from Anhui Institute of Chemical Engineering were used as received without any purification. Three commercial HALS photostabilizers:

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Poly[2-*N,N'*-di(2,2,6,6-tetramethyl-4-piperidiny)-hexanediamine-4-(1-amino-1,1,3,3-tetramethyl-butane)sym-tri-*ar*ine] (Chimassorb 944), Bis(2,2,6,6-tetramethyl-4-piperidiny)sebacate (Tinuvin 770), and Tinuvin 783, which is a mixture of 50% Chimassorb 944 and 50% Tinuvin 622 (polyester of succinic acid with *N*- β -hydroxy-ethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine), were supplied by the Ciba-Geigy Corporation.

2.2. Sample preparation

LDPE resin with the desired amounts of additives was mixed at 150°C for 10 min using a two-roll mill. After mixing, the mixture was hot-pressed to sheets of suitable thickness at 150°C for 5 min using a press.

2.3. Sample irradiation

Samples were irradiated in a UV-CURE device constructed in this laboratory [4]. In the normal photocross-linking experiments, LDPE samples were irradiated by a high-pressure mercury lamp (Philips HPM 15), operated at 2 kW, at a distance of 10 cm from the surface of sample. These samples were defined as the XLPE samples.

In the deoxidation experiments, the irradiation process of PE was divided into two steps. The sample was pre-irradiated first for a given time by a low-pressure mercury (LPM) lamp (type WXZ-1 made in China, 40 w, the main emission wavelength covered the 254 nm range), and then immediately irradiated by a Philips HPM 15 lamp for 40 s to prepare the cross-linked samples. Such prepared samples were defined as the pre-XLPE samples.

2.4. Thermal aging

The XLPE samples were exposed in an oven (type XG-CN, made in Nantong, China) at 135°C for 7 days. The fluctuant range of temperature was kept within 0.2°C.

2.5. Measurements

2.5.1. FTIR spectra

The FTIR Spectra were recorded with a Nicolet MAGNA-IR 750 spectrometer. In order to minimize errors from sample thickness, the 1895 cm⁻¹ peak from the C–H deformation mode of PE was used as an internal reference in this study. The relative absorbance intensity of C=O at 1716 cm⁻¹ was expressed by carbonyl index A_{1716}/A_{1895} , where A_{1716} and A_{1895} were the absorbencies at 1716 cm⁻¹ and 1895 cm⁻¹, respectively.

2.5.2. XPS spectra

The XPS spectra were recorded with a VG ESCALAB MK II spectrometer, using Al k_{α} excitation radiation ($h\nu = 1253.6$ eV).

3. Results and discussion

3.1. Surface photo-oxidation of XLPE

Fig. 1 shows the FTIR spectra of samples UV-irradiated with a HPM-15 lamp for different irradiation times. The main changes of spectra are found in the 3400 cm⁻¹ and 1700 cm⁻¹ regions from the hydroxyl and carbonyl groups, respectively. The broad absorption band in the 3400 cm⁻¹ region is due to hydrogen-bonded hydroxyl groups (alcohols, hydroperoxides and carboxylic acids). The two narrow and weak absorption peaks at 3605 and 3550 cm⁻¹ are attributed to non-hydrogen-bonded alcohols and hydroperoxides [12], respectively. The small peak at 1666 cm⁻¹ is the carbonyl absorption of photoinitiator benzophenone. Its intensity decreased rapidly with increasing irradiation time. The absorption peak of oxidation products from the 10 s sample appeared at 1722 cm⁻¹, which is mainly due to the ketone groups. Its absorption intensity increased rapidly with increasing irradiation time, as shown in the 20–80 s samples of Fig. 1. At the same time the absorption peak of the ketone groups was shifting to 1716 cm⁻¹ because of the overlapping of the peak (1710 cm⁻¹) from the growing carboxylic acid groups. For the 160 s sample, two new shoulder peaks of 1780 and 1730 cm⁻¹ appeared at the absorption band of carbonyl groups, which have been assigned to the lactone [13] and aldehyde compounds, respectively. The 1176 cm⁻¹ peak of the lactone groups was also observed from the 160 s sample. On the other hand, the unsaturated group also reflects the photo-oxidation degradation in the XLPE samples. The increases of absorption intensities of 1645 and 909 cm⁻¹ peaks in the FTIR spectra indicate the formation of unsaturated vinyl groups [14].

Fig. 2 shows the C_{1s} XPS spectra of the XLPE samples UV-irradiated with a Philips HPM 15 lamp for different irradiation times. The strong peak at 285.0 eV is due to the C_{1s} electron from the C–C and C–H bonds of PE. The intensity of the small peak appeared at

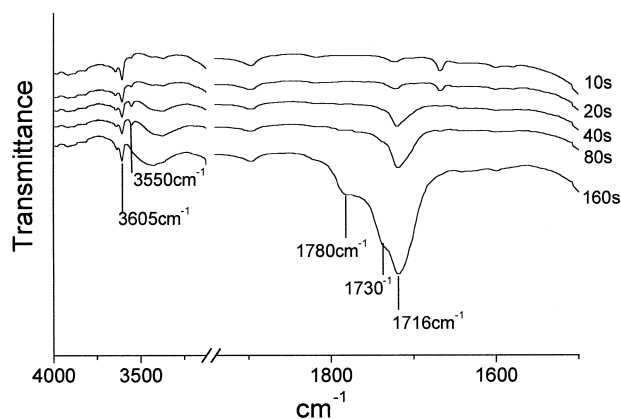


Fig. 1. FTIR spectra of the XLPE samples irradiated with a Philips HPM-15 lamp for different times.

286–290 eV in the C_{1s} band and increases with increasing irradiation time, which indicates the formation of surface photo-oxidation products, such as $-\underline{C}H_2-O-$, $-\underline{C}(=O)-$, and $-\underline{C}(=O)-O-$ groups.

3.2. Thermal-oxidation aging of XLPE

The surface photo-oxidation taking place during the photocross-linking of PE has a significant effect on the thermal-oxidation aging property of XLPE. The XPS spectra of C_{1s} and O_{1s} for the XLPE samples with different irradiation times after thermal-oxidation aging for 168 h at 135°C are shown in Fig. 3. It can be seen from the C_{1s} peaks in Fig. 3 that the oxidation products after thermal aging increase apparently with increasing UV-irradiation time of XLPE samples. The oxidation products B, C and D marked by broken lines obtained by computer separating peaks of C_{1s} bands appear at 286.5, 288.0 and 289.0 eV, which have been assigned to the $-\underline{C}H_2-O-$, $-\underline{C}(=O)-$, and $-\underline{C}(=O)-O-$ groups, respectively. The O_{1s} peaks in Fig. 3 also show that the oxidation products increase quickly with the irradiation time of XLPE samples. The O_{1s} peak of 40 s sample mainly appeared at 532.5 eV, which is due to the $-\underline{C}(=O)-$ and $-\underline{C}H_2-O-$ groups. The shoulder peaks of O_{1s} appeared at 534.2 eV for the 80 s and 160 s samples are assigned to the $-\underline{C}(=O)-O-$ groups.

The stoichiometric O/C ratios obtained from the XPS spectra are used to characterize the degree of surface oxidation. The O/C data of XLPE samples before and after thermal aging are listed in Table 1. The O/C values of 40s and 80s samples before aging were 0.08 and 0.09,

respectively. But the O/C value increased rapidly to 0.20 when the irradiation time of sample prolonged to 160 s, which almost approaches the 0.24 value of the 40 s sample after thermal-aging. These data give the positive evidence that the degree of surface photo-oxidation in the XLPE sample is of crucial importance for the thermal-oxidation property of XLPE materials.

3.3. Surface photostabilization of XLPE

3.3.1. Deoxidation by pre-irradiation by a LPM lamp

The UV light of 254 nm from the low-pressure mercury (LPM) lamp can scavenge the oxygen absorbed on a polymer surface by photochemical reactions. The absorption and diffusion of oxygen on the sample surface play an important role in the photo-oxidation reaction of polymers. So, the photoinitiated cross-linking of PE is usually carried out in an inert atmosphere because of oxygen suppressing the cross-linking process and protecting the PE samples from the surface oxidation. However, it is costly and not convenient for industrial applications of a photocross-linking technique. Detaching the oxygen absorbed on the PE surface before photocross-linking can be carried out by a suitable pre-irradiation of a LPM lamp, as described in the patent [8].

In the deoxidation experiments, all pre-XLPE samples were irradiated for 40 s by a HPM lamp after being pre-irradiated for a given time by a LMP lamp. The surface photo-oxidation of various samples has been analyzed by FTIR and XPS methods. The carbonyl index A_{1716}/A_{1895} obtained from FTIR spectra is used to characterize the degree of oxidation, as described in the experimental section. Fig. 4 shows the changes of carbonyl index of the pre-XLPE samples with different pre-irradiation times. It can be seen that 10 s is the best choice of pre-irradiation time because of its lowest carbonyl index among all the pre-XLPE samples. The 5 s pre-irradiation was not enough for detaching all the oxygen absorbed on the PE surface. But the carbonyl index increased rapidly when the pre-irradiation time is longer than 10 s, as shown in Fig. 4.

The XPS studies show that the C_{1s} and O_{1s} peaks of sample without UV irradiation appeared at 285.0 and 532.5 eV, respectively. The O_{1s} peak of samples without UV irradiation appeared at 532.5 eV and was due to the oxidation products formed from the storage and processing of polymer. New C_{1s} and O_{1s} shoulder peaks appeared at 287.0 and 534.2 eV after UV irradiation, respectively, which indicates the formation of surface oxidation products associated with carbon and oxygen atoms. The relative intensities (RI) of oxidation products can be defined as the values of $RI = I_{287}/I_{285}$ and $I_{534.2}/I_{532.5}$, respectively. The comparison of RI data of surface oxidation products obtained by the C_{1s} and O_{1s} XPS spectra of different samples are given in Table 2. As we can see from Table 2, the RI values of C_{1s} and

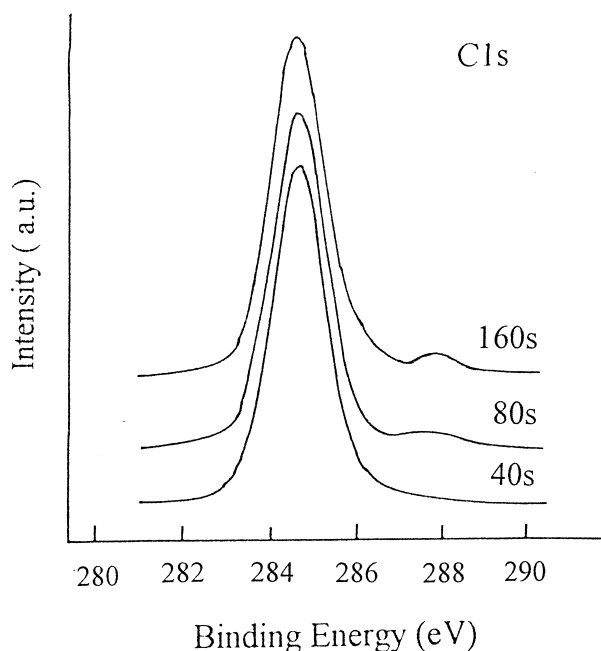


Fig. 2. C_{1s} XPS spectra of the XLPE samples irradiated with a Philips HPM-15 lamp for different times.

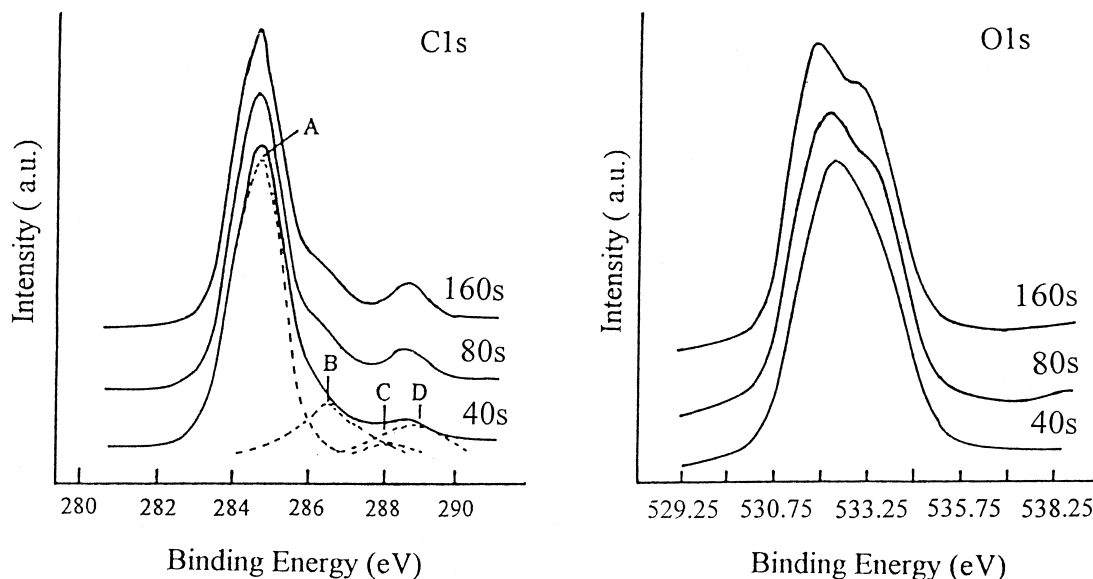


Fig. 3. C_{1s} and O_{1s} XPS spectra of the XLPE samples after the thermal aging at 135°C for 168 h.

O_{1s} in the XLPE sample irradiated for 40 s by the HPM lamp increase very fast to 4.33 and 2.92, respectively, compared with the corresponding zero values from the sample with no irradiation. Apparently, the C_{1s} and O_{1s} data from the three pre-XLPE samples in Table 2 show that the 10 s is an optimum pre-irradiation time because the C_{1s} (287.0 eV) and O_{1s} (534.2 eV) peaks characteristic of surface oxidation products disappeared after 10 s

Table 1
O/C values of the XLPE samples before and after thermal aging measured by XPS

Samples	UV irradiation time		
	40 s	80 s	160 s
O/C before aging	0.08	0.09	0.20
O/C after aging	0.24	0.28	0.29

pre-irradiation by the LPM lamp. This result is in good agreement with those obtained by the FTIR spectra (see Fig. 4).

Table 2
The XPS relative intensities (RI) of surface photo-oxidation products determined from the pre-XLPE samples by comparing with the sample of no irradiation

Irradiation conditions	RI obtained from the I_{287}/I_{285} values of C_{1s} peaks	RI obtained from the $I_{534.2}/I_{532.5}$ values of O_{1s} peaks
No irradiation	0	0
^a 0 + 40	4.33	2.92
5 + 40	4.88	0.69
10 + 40	0	0
20 + 40	8.36	10.05

^a The former item is the pre-irradiation time of a LMP lamp, the latter item is the UV-irradiation time of a HPM lamp.

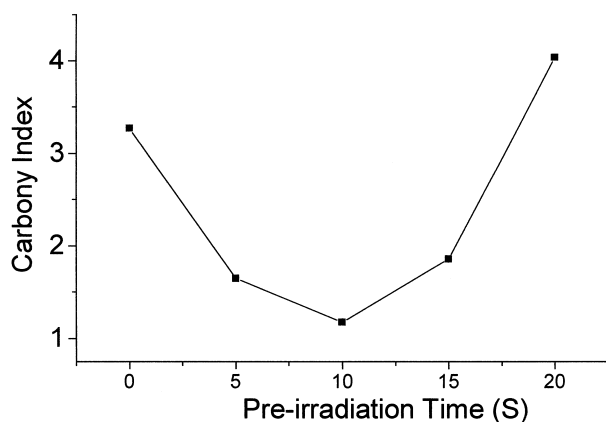


Fig. 4. Changes of carbonyl index in the pre-XLPE samples with different pre-irradiation times of LMP lamp.

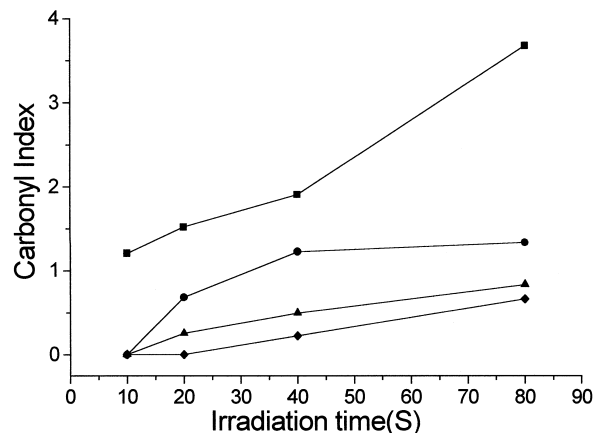


Fig. 5. Comparison of photostabilization of different HALS: no HALS (■); Tinuvin 783 (◆); Tinuvin 770 (▲); Chimassorb 944 (●).

3.3.2. Photostabilization of HALS on the surface of XLPE

Photostabilizer HALS can effectively protect polymer from the photo-oxidation. In photoinitiated cross-linking of polyethylene, photostabilizer HALS was used to protect the XLPE materials from the surface photo-oxidation. The efficiency of photostabilizer can be estimated by carbonyl index (A_{1716}/A_{1895}) obtained from FTIR spectra. Fig. 5 shows the changes of carbonyl indexes of different samples with the irradiation time by the HPM lamp. It can be seen that the carbonyl indexes of samples with HALS are much lower than that of samples without HALS. Tinuvin 783 is the most efficient among the three kinds of HALS stabilizers used in the present study, which might be due to a synergistic

effect because it is a mixture of two kinds of HALS stabilizers Chimassorb 944 and Tinuvin 622.

3.4. Surface photo-oxidation mechanism of photocross-linked XLPE

During UV irradiation, the excited triplet state of BP abstracts hydrogen from the PE chain (PH) to form ketyl ($K\bullet$) and polymer alkyl ($P\bullet$) radicals. At the same time of crosslink formation, the $P\bullet$ radicals can easily react with oxygen absorbed on the PE surface to produce polymer peroxy ($POO\bullet$) radicals. These $POO\bullet$ radicals react further with PE to form the hydroperoxides and hydroxyl compounds.

Hydroperoxides are the most important intermediates in the surface photo-oxidation process of PE. Under UV irradiation, hydroperoxides decompose quickly to form various oxidation products, such as ketone, carboxylic, lactone, and aldehydes etc. The reaction processes for these oxidation products formed on the XLPE surface are shown in Fig. 6, together with the corresponding IR absorption peaks, as described in the above sections.

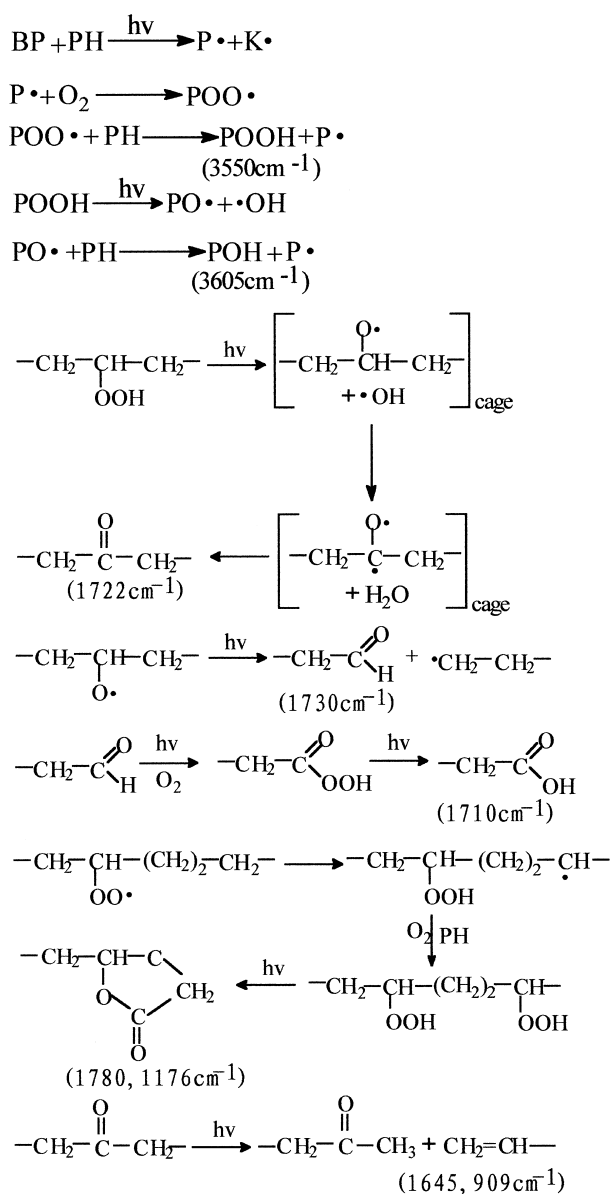


Fig. 6. Formation mechanism of various surface oxidation products during the photoinitiated cross-linking of PE.

4. Conclusions

1. The surface photo-oxidation in the photoinitiated cross-linking of PE increases with increasing irradiation time. The main photo-oxidation products are hydroperoxides and various carbonyl groups.
2. The pre-irradiation by the LPM lamp is an efficient method of protecting the photocross-linked XLPE from surface photo-oxidation during the photocross-linking process. The FTIR and XPS data show that 10 s are an optimum time for detaching the oxygen absorbed on the PE surface under the experimental conditions of this work.
3. Using photostabilizer HALS in the photoinitiated cross-linking of PE is an efficient method against the surface photo-oxidation. Tinuvin 783 is the most efficient one among the three kinds of HALS stabilizers.

Acknowledgements

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References

- [1] Qu BJ, Shi WF, Rånby B. Photocross-linking of LDPE and its application for wire and cable. *J Photopolym Sci Technol* 1989;2:269.
- [2] Chen YL, Rånby B. Photocrosslinking of polyethylene. I. Photoinitiators, crosslinking agent, and reaction kinetics. *J Polym Sci Part A: Polym Chem* 1989;27:4051.

- [3] Yan Q, Xu WY, Rånby B. Photoinitiated crosslinking of low density polyethylene. I. Reaction and kinetics. *Polym Eng Sci* 1991;31:1561.
- [4] Qu BJ, Rånby B. Photocrosslinking of low-density polyethylene. I. Kinetics and reaction parameters. *J Appl Polym Sci* 1993;48:701.
- [5] Qu BJ, Liang RY, Shi WF, Jin SZ, Xu YH. Chinese Patent 1991, 91208128.9.
- [6] Rånby B. Eur Patent 1992, 490854.
- [7] Qu BJ, Shi WF, Liang RY, Jin SZ, Xu YH, Wang ZH. Photocrosslinking of polyethylene for production of thin wall insulated wire. *Polym Eng Sci* 1995;35(12):1005.
- [8] Qu BJ, Xu YH, Liang RY, Shi WF, Wu, QH. Chinese Patent 1998, Appl No. 98123197.7.
- [9] Qu BJ, Xu YH, Shi WF, Rånby B. Photoinitiated cross-linking of low-density polyethylene. 6. Spin-trapping ESR studies on radical intermediates. *Macromolecules* 1992;25:5215.
- [10] Qu BJ, Xu YH, Shi WF, Rånby B. Photoinitiated cross-linking of low-density polyethylene. 7. Initial radical reactions with model compounds studied by spin-trapping ESR spectroscopy. *Macromolecules* 1992;25:5220.
- [11] Qu BJ, Qu X, Xu YH, Jacobsson U, Rånby B. *Macromolecules* 1997;30:1408.
- [12] Lacoste J, Carlsson DJ. Gamma, photo, and thermal-initiated oxidation of linear low density polyethylene: a quantitative comparison of oxidation products. *J Polym Sci Part A: Polym Chem* 1992;30:493.
- [13] Lacoste J, Arnaud R, Singh RP, Lemaire J. *Makromol Chem* 1988;189:651.
- [14] Torikai A, Takeuchi A, Nagaya S, Fueki K. Photodegradation of polyethylene: effect of crosslinking on the oxygenated products and mechanical properties. *Polym Photochem* 1986;7:199.